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# CYCLOMETALATION AT CARBON ADJACENT TO OXYGEN IN PLATINUM(II) AND IRIDIUM(I) PHOSPHINE COMPLEXES

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## Summary

Heating *trans*-$PtCl_2(t\text{-}Bu_2PCH_2OCH_3)_2$ at 125°C in 2-methoxyethanol yields a cyclometalated derivative, $PtCl(t\text{-}Bu_2PCH_2OCH_2)(t\text{-}Bu_2PCH_2OCH_3)$. Adding excess NaI and 1,8-bis(dimethylamino)naphthalene accelerates the reaction and gives the iodide-substituted analog. Under the same conditions, *trans*-$PtCl_2(t\text{-}Bu_2POCH_2CH_3)_2$ is also metalated at the methyl carbon atom. However, the slower rate of this reaction indicates that an α-oxygen atom has an electronic accelerating effect on the metalation process. Neither $t\text{-}Bu_2POCH_3$ nor $t\text{-}Bu_2PCH_2CH_2OCH_3$ give platinum(II) cyclometalated complexes; four- or six-membered chelate ring formation appears to be unfavorable. The $t\text{-}Bu_2PCH(CH_3)OCH_3$ ligand also does not yield a platinum(II) metalated derivative. However, $[IrCl(COT)_2]_2$ (COT = cyclooctene) reacts at 25°C with both $t\text{-}Bu_2PCH_2OCH_3$ and $t\text{-}Bu_2PCH(CH_3)OCH_3$, to form iridium(III) metalated complexes by oxidative addition to the methyl C—H bond. These coordinatively unsaturated compounds react with CO, yielding octahedral iridium(III) carbonyl hydride complexes.

## Introduction

Addition of carbon—hydrogen bonds to transition metal complexes may have great potential for catalytic applications [1]. This reaction has been widely studied in the cyclometalation process, in which an organic ligand undergoes intramolecular metalation [2]. Most of these reactions involve addition to an aromatic ring or groups attached to it, although there are a few examples of aliphatic carbon cyclometalation [3—7]. We have now investigated the cyclometalation of aliphatic carbon—hydrogen bonds α to an oxygen atom in phosphine ligands. The heteroatom was expected to have an electronic influence on the metalation process, and may be useful in subsequent reactions of the metalated complex. There are previous reports of alkoxy group cyclometalation;

these groups were substituents on a phenyl ring, and formed six-membered metalated rings [8,9]. Since five-membered ring formation is normally favored, it is not possible to compare those results with findings for non-oxygen-containing analogs. Thus the influence of the oxygen atom was unknown.

Addition of a metal atom to C—H bonds $\alpha$ to oxygen is also apparently involved in metal complex catalyzed transfer of hydrogen from ethers to olefins [10] or aldehydes [11]. However, in these processes a major function of the oxygen atom may be to provide a coordination site for the metal immediately prior to C—H addition.

## Results and discussion

Bulky ligand substituents have been found by other workers to promote cyclometalation of phosphorus ligands [4,12,13]. The present studies have therefore been carried out largely with phosphine ligands of the type t-$Bu_2$-P—R—$OCH_3$, where R represents various groups linking P and O. Most of these ligands are new and were prepared by methods described in the Experimental section or elsewhere [14].

### *Platinum complexes*

Phosphine complexes of platinum(II) were prepared either from $PtCl_2(C_6H_5CN)_2$ or from $Na_2PtCl_4$, as described below. All of the t-butyl substituted phosphines form complexes of *trans* geometry, as indicated by their yellow color, the single $\nu$(Pt—Cl) infrared band, and by the very strong phosphorus—phosphorus coupling evident in the $^1$H NMR spectra of the t-butyl protons [4].

When the yellow $PtCl_2$(t-$Bu_2PCH_2OCH_3)_2$ complex is heated at 124—175°C in 2-methoxyethanol, diglyme, or decalin, it is converted within a few hours to a colorless cyclometalated complex (eq. 1). The production of HCl has been confirmed by trapping the evolved gas in $H_2O$ and testing with pH paper and


(1)

L = t-$Bu_2PCH_2OCH_3$

$AgNO_3$. An infrared band of the starting complex at 1105 $cm^{-1}$, attributed to the asymmetric C—O—C stretching mode, $\nu$(COC), decreases in intensity and shifts to 1100 $cm^{-1}$ upon metalation. Simultaneously a new band appears at 1055 $cm^{-1}$ which is assigned to $\nu$(COC) of the cyclometalated ring. The $\nu$(Pt—Cl) band of the starting complex shifts upon metalation from 340 $cm^{-1}$ to 260 $cm^{-1}$, a value typical for Cl *trans* to carbon in platinum(II) complexes [15]. The $^1$H NMR spectrum of the product also supports the assigned structure. The t-butyl groups (which show a triplet for the starting complex because of strong P—P coupling) appear as a doublet in $CDCl_3$ solvent. However, in $C_6D_6$ they are shown to be two sets of doublets at $\tau$ 8.55 and 8.62, both $J$(PH) = 13 Hz. All of the other protons are also observed, with appropriate P—H and Pt—H couplings.

The same starting complex, $PtCl_2(t\text{-}Bu_2PCH_2OCH_3)_2$, when heated to 124°C in 2-methoxyethanol containing excess NaI and 1,8-bis(dimethylamino)naphthalene yields, within 30 min, the cyclometalated $PtI(t\text{-}Bu_2PCH_2OCH_2)(t\text{-}Bu_2PCH_2OCH_3)$ product. The accelerating effect of the iodide ligand relative to chloride has been previously noted, and ascribed to either a steric or an electronegativity effect [4]. The 1,8-bis(dimethylamino)naphthalene serves to neutralize the acid formed on metalation, since we have found that the reaction of eq. 1 can be reversed by using excess anhydrous HCl.

The palladium complex $PdCl_2(t\text{-}Bu_2PCH_2OCH_3)_2$ was stable for long periods under conditions which gave complete metalation of the Pt analog; no cyclometalated species could be detected.

The $PtCl_2(t\text{-}Bu_2POCH_2CH_3)_2$ complex does undergo metalation upon heating to 124°C in 2-methoxyethanol containing excess NaI and the naphthalene base, yielding $PtI(t\text{-}Bu_2POCH_2CH_2)(t\text{-}Bu_2POCH_2CH_3)$; approximately 2 h was required for the reaction.

Shaw and coworkers have reported that $PtCl_2(t\text{-}Bu_2PCH_2CH_2CH_3)_2$ yields a cyclometalated product after heating with LiBr in refluxing 2-methoxyethanol for four days [4]. It appears, therefore, that there is a substantial activating effect of the oxygen atom, apparently electronic in nature, in the series $t\text{-}Bu_2PCH_2OCH_3 > t\text{-}Bu_2POCH_2CH_3 > t\text{-}Bu_2PCH_2CH_2CH_3$.

Because of this activating effect of the oxygen atom, it was hoped that cyclometalation could be achieved in platinum(II) complexes of $t\text{-}Bu_2POCH_3$ and $t\text{-}Bu_2PCH_2CH_2OCH_3$, in which normally unfavored four- or six-membered rings would be formed upon C—H addition. However, no evidence for cyclometalation was ever observed in reactions of these complexes; it appears that the steric factors which disfavor four- or six-membered ring formation predominate over the oxygen activating effect.

Surprisingly, platinum(II) complexes of $t\text{-}Bu_2PCO_2CH_3$, which could form five-membered rings upon C—H metalation, were very stable even upon heating for extended periods. Reasons for this unreactivity are unclear. Analogous complexes of $t\text{-}Bu_2PCH_2CO_2CH_3$ do give metalated products, but these are O-metalated $PtX(t\text{-}Bu_2CH_2C(O)O)(t\text{-}Bu_2PCH_2CO_2CH_3)$ derivatives analogous to those recently reported by Shaw et al. [16]. Heating $PtCl_2(Ph_2PCO_2CH_3)_2$ above 150°C in decalin gave an insoluble product which did not contain ester groups and was not investigated further.

Unusual behavior was observed upon heating $PtCl_2[t\text{-}Bu_2PCH(CH_3)OCH_3]_2$. The major product isolated (>30% yield) from the reaction mixture was $PtCl_2(t\text{-}Bu_2PH)_2$ [17] presumably formed according to eq. 2. This reaction appears to be acid-catalyzed, perhaps by small amounts of HCl produced in a metalation

$$PtCl_2[t\text{-}Bu_2PCH(CH_3)OCH_3]_2 \rightarrow PtCl_2(t\text{-}Bu_2PH)_2 + 2\ CH_2{=}CHOCH_3 \qquad (2)$$

process, since addition of 1,8-bis(dimethylamino)naphthalene inhibits the conversion. No metalated products could be isolated from these reactions, although spectroscopic evidence suggests their formation in small amounts. The related $PtCl_2[Et_2PCH(CH_3)OCH_3]_2$ complex is quite stable under the same conditions, both to metalation and to decomposition of the type in eq. 2.

The reluctance of platinum(II) complexes of the $t\text{-}Bu_2PCH(CH_3)OCH_3$ ligand to undergo cyclometalation may be a result of steric interaction between

the bulky —$CH(CH_3)OCH_3$ substituent and a halide ligand on the metal, which could force the phosphine ligand into a conformation unfavorable for metalation. Support for this view arises from the observation (vide infra) that an iridium(I) monohalide species, in which such interactions are less important, converts readily to a cyclometalated complex of this phosphine.

*Iridium complexes*

Reaction of a hexane suspension of $[IrCl(COT)_2]_2$ (COT = cyclooctene) with excess t-$Bu_2PCH_2OCH_3$ at room temperature gives a red solution after several hours, from which good yields of a dark red crystalline product can be obtained by concentrating and cooling. The $^1H$ NMR spectrum shows no coordinated cyclooctene, and only one —$OCH_3$ group remains. Some broadening of peaks is observed, suggestive of fluxional behavior. The elemental analyses are consistent with the formula IrHCl(t-$Bu_2PCH_2OCH_2$)(t-$Bu_2PCH_2OCH_3$), a coordinatively unsaturated species. The complex does, in fact, react very rapidly with added ligands. Thus bubbling CO through a hexane solution of the complex gives an immediate color change from red to pale yellow, and a complex of the formula Ir(CO)HCl(t-$Bu_2PCH_2OCH_2$)(t-$Bu_2PCH_2OCH_3$) is isolated by concentrating and cooling the solution (eq. 3). The infrared spectrum of this com-

$$1/2\ [IrCl(COT)]_2 \xrightarrow[2.\ CO]{1.\ 2\ t\text{-}Bu_2PCH_2OCH_3} \text{t-}Bu_2P(CH_2{-}O)(H)(CH_2)(Cl)(CO)Ir \cdot \text{t-}Bu_2PCH_2OCH_3 \qquad (3)$$

plex shows distinct $\nu$(IrH) and $\nu$(CO) bands, and two $\nu$(COC) peaks are observed as for PtX(t-$Bu_2PCH_2OCH_2$)(t-$Bu_2PCH_2OCH_3$). The $^{13}C$ NMR spectrum is also quite similar to that of the platinum complex. The $^1H$ NMR spectrum has a hydride resonance at $\tau$ 18.0, which appears as a pseudotriplet of doublets because of coupling to two non-equivalent phosphorus nuclei and, presumably, one of the non-equivalent Ir—$CH_2$ protons.

The t-$Bu_2PCH(CH_3)OCH_3$ ligand also reacts with $[IrCl(COT)_2]_2$ at 25°C, yielding a dark red coordinatively unsaturated complex, IrHCl[t-$Bu_2PCH(CH_3)OCH_2$]-[t-$Bu_2PCH(CH_3)OCH_3$]. Further reaction of this complex with CO also gives the corresponding carbonyl complex.

Although the exact mechanism by which an oxygen atom activates an adjacent C—H bond toward metalation is not clear, it might be expected that the increased electrophilicity of the carbon atom should render it more susceptible to oxidative addition. Since iridium(III) products are obtained, metalation reactions involving iridium(I) are oxidative addition processes. It seems probable that the platinum(II) reactions proceed by a similar pathway, yielding transient platinum(IV) species which reductively eliminate HX. However, a four-center concerted mechanism is also possible, which could be aided as well by the oxygen atom.

## Experimental section

*General information*

Infrared spectra were recorded on Perkin—Elmer 237 or Beckman IR-20A instruments. $^1$H NMR spectra were obtained with Varian A-60A, Varian EM-360, and Perkin—Elmer R-12 spectrometers. $^{13}$C NMR spectra were measured on the Varian XL-100. Elemental analyses (C, H, and N) were performed by Mr. J.T. Hildebrand of the Union Carbide Analytical Section. Other analyses (phosphorus, halogen) were performed by Schwarzkopf Microanalytical Labs, Woodside, N.Y.

Bis(benzonitrile)platinum(II) chloride and the palladium analog were prepared by heating the metal(II) chlorides in benzonitrile [18]. Di-t-butylphosphine [19], di-t-butylchlorophosphine [20], and $[IrCl(COT)_2]_2$ [21] were prepared according to literature procedures. Tetrahydrofuran (THF) and diethyl ether were distilled from $LiAlH_4$ immediately before use. 1,4-Dioxane was distilled from Na/K alloy. Other reagent grade chemicals were used without further purification. Reactions and operations were routinely performed under a nitrogen atmosphere using Schlenk techniques. The air-sensitive phosphines were analyzed as their $PtCl_2L_2$ derivatives.

*t-Bu$_2$PCH$_2$OCH$_3$*

Phenyllithium (60 ml of 1.8 *M* solution in ether/benzene, 108 mmol) was added slowly to t-Bu$_2$PH (15.6 g, 107 mmol) in 100 ml THF. After cooling to 25°C, this solution was slowly transferred by cannula (double-tipped needle) to a solution of $ClCH_2OCH_3$ (9 ml, 119 mmol) in 1000 ml diethyl ether. The solvents were removed by distillation at atmospheric pressure. Vacuum distillation gave 13.64 g (67%) of the product, b.p. 112—115°C/17 mmHg; IR (neat): $\nu$(COC) 1090 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\tau$ 6.18 (d, $^2J$(PH) 3.5 Hz, 2H, $CH_2$), 6.65 (s, 3H, $CH_3$), 8.83 ppm (d, $^3J$(PH) 11 Hz, 18H, t-Bu). Anal.: Found: C, 39.62; H, 8.02. [P-t-Bu$_2$($CH_2OCH_3$)$CH_3$]I calcd.: C, 39.76; H, 7.83%.

*t-Bu$_2$POCH$_3$*

A suspension of $LiOCH_3$ (4.0 g, 105 mmol) in 350 ml THF was refluxed with t-Bu$_2$PCl (16.59 g, 92 mmol) for 28 h, and the solvent was then distilled off. The product (10.34 g, 64%) was collected by vacuum distillation, b.p. 63—64°C/8 mmHg. $^1$H NMR ($CDCl_3$): $\tau$ 6.56 (d, $^3J$(PH) 11.3 Hz, 3H, $OCH_3$), 8.98 ppm (d, $^3J$(PH) 10.7 Hz, 18H, t-Bu).

*t-Bu$_2$POCH$_2$CH$_3$*

A solution of $LiOCH_2CH_3$ (6.7 g, 129 mmol) and t-Bu$_2$PCl (12.5 g, 69 mmol) in 300 ml THF was refluxed for 48 h. Solvent was removed by distillation at atmospheric pressure, and the product (7.42 g, 56%) was collected by vacuum distillation, b.p. 41—42°C/0.5 mmHg. $^1$H NMR ($CDCl_3$): $\tau$ 6.22 (quintet, $^3J$(HH) 7 Hz, $^3J$(PH) 7 Hz, 2H, $POCH_2$), 8.78 (t, $^3J$(HH) 7 Hz, 3H, $CH_3$), 8.92 ppm (d, $^3J$(PH) 11.5 Hz, 18H, t-Bu).

*t-Bu$_2$PCO$_2$CH$_3$*

Di-t-butylphosphine (11.0 g, 75 mmol) was stirred in 100 ml THF while

phenyllithium (42 ml of 1.8 *M* solution in ether/benzene, 76 mmol) was added dropwise by syringe. This solution was allowed to cool to room temperature and transferred by cannula to a solution of methyl chloroformate (7.3 g, 74 mmol) in 25 ml benzene, with stirring and ice-water cooling, over a period of 45 min. After stirring an additional hour at 25°C, the solution was distilled under vacuum to yield the yellow product (7.15 g, 58%), b.p. 70°C/1.4 mmHg. IR (neat): $\nu$(CO) 1690, $\nu$(COC) 1120 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\tau$ 6.28 (s, 3H, $OCH_3$), 8.73 ppm (d, $^3J$(PH) 12 Hz, 18H, t-Bu).

*t-$Bu_2PCH_2CO_2CH_3$*

A solution of t-$Bu_2PH$ (6.0 g, 41 mmol) and $BrCH_2CO_2CH_3$ (6.3 g, 41 mmol) in 50 ml acetone was stirred 16 h at 25°C. The resulting white bulky solid was washed with pentane and dissolved in 50 ml methanol. A solution of $NaOCH_3$ (2.60 g, 48 mmol) in 20 ml methanol was then added. The mixture was concentrated to about 15 ml under vacuum, diluted with 50 ml diethyl ether, and filtered through Celite. Distillation at atmospheric pressure removed the solvent, and continued distillation under vacuum gave the product (4.50 g, 50%), b.p. 88—93°C/1 mmHg. $^1H$ NMR ($CDCl_3$): $\tau$ 6.35 (s, 3H, $OCH_3$), 7.55 (d, $^2J$(PH) 3 Hz, 2H, $PCH_2$), 8.85 ppm (d, $^3J$(PH) 11 Hz, 18H, t-Bu).

*$Ph_2PCO_2CH_3$*

Diphenylchlorophosphine (10.0 g, 45 mmol) was refluxed in 150 ml 1,4-dioxane with Na metal (8.0 g, 348 mmol) for 7 h. Then 160 ml THF was added and the orange solution was filtered through Celite and transferred to an addition funnel. This solution was added dropwise to methyl chloroformate (6.1 g, 65 mmol) in 50 ml THF over a period of 5 h. The mixture was refluxed 30 min, filtered, and distilled under vacuum to yield the product (7.0 g, 63%), b.p. >170°C/0.15 mmHg. IR (neat): $\nu$(CO) 1695, $\nu$(COC) 1140 $cm^{-1}$. $^1H$ NMR ($CCl_4$): $\tau$ 2.70 (m, 5H, $C_6H_5$), 6.45 ppm (s, 3H, $CH_3$).

*$PtCl_2$(t-$Bu_2PCH_2OCH_3$)$_2$*

A mixture of $PtCl_2(NCC_6H_5)_2$ (3.05 g, 6.46 mmol) and t-$Bu_2PCH_2OCH_3$ (2.50 g, 13.1 mmol) in 50 ml methanol was stirred at 25°C for 30 min, causing most of the platinum complex to dissolve. The solution was filtered and refluxed for 6 h, then slowly cooled to 25°C. The resulting yellow crystalline product (3.00 g, 72%) was collected by filtration and vacuum-dried: IR ($CH_2Cl_2$): $\nu$(COC) 1105 $cm^{-1}$, (Nujol) $\nu$(PtCl) 340 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\tau$ 5.68 (s, $^3J$(PtH) 17 Hz, 4H, $CH_2$), 6.62 (s, 6H, $CH_3$), 8.46 ppm (t, $^3J$(PH) + $^5J$(PH) 13.5 Hz, 36H, t-Bu); $^{13}C$ NMR ($CDCl_3$): $\delta$ 61.63 (t, $^1J$(PC) + $^3J$(PC) 75.6 Hz, $^2J$(PtC) 25.1 Hz, $CH_2$), 60.37 (t, $^3J$(PC) + $^5J$(PC) 20.8 Hz, $CH_3$), 36.37 (t, $^1J$(PC) 40.3 Hz, $\underline{C}(CH_3)_3$), 30.60 ppm (s, $C(\underline{C}H_3)_3$). Anal.: Found: C, 35.81; H, 6.05. Calcd.: C, 35.61; H, 6.23%.

*$PtCl_2$(t-$Bu_2POCH_2CH_3$)$_2$*

A suspension of $PtCl_2(NCC_6H_5)_2$ (1.5 g, 3.18 mmol) in 30 ml ethanol was treated with t-$Bu_2POCH_2CH_3$ (1.3 g, 6.84 mmol) and stirred 30 min. The solution was filtered and refluxed 16 h. Cooling to 25°C gave the light yellow product (1.72 g, 84%). $^1H$ NMR ($CDCl_3$): $\tau$ 5.85 (q of t, $^3J$(HH) 6.5 Hz, $^3J$(PH) +

$^5J$(PH) 5.0 Hz, 4H, $OCH_2$), 8.50 (t, $^3J$(PH) + $^5J$(PH) 14 Hz, 36H, t-Bu), 8.70 ppm (t, $^3J$(HH) 6.5 Hz, 6H, $CH_3$). Anal.: Found: C, 37.04; H, 7.27. Calcd.: C, 36.92; H, 7.08%.

*$PtCl_2(t\text{-}Bu_2POCH_3)_2$*

A suspension of $PtCl_2(NCC_6H_5)_2$ (2.0 g, 4.24 mmol) in 40 ml methanol was stirred at 25°C for 1 h with $t\text{-}Bu_2POCH_3$ (1.5 g, 8.52 mmol). The solution was then filtered and refluxed 14 h. Concentration of the solution under vacuum and cooling gave pale yellow crystals (1.54 g, 59%). $^1$H NMR ($CDCl_3$): $\tau$ 6.08 (t, $^3J$(PH) + $^5J$(PH) 22.0 Hz, 6H, $OCH_3$), 8.50 ppm (t, $^3J$(PH) + $^5J$(PH) 14.0 Hz, 36H, t-Bu). Anal.: Found: C, 34.99; H, 6.91. Calcd.: C, 34.95; H, 6.80%.

*$PtCl_2[t\text{-}Bu_2PCH(CH_3)OCH_3]_2$*

A mixture of $Na_2PtCl_4 \cdot 4\ H_2O$ (0.90 g, 1.98 mmol), $t\text{-}Bu_2PCH(CH_3)OCH_3$ (1.0 g, 4.90 mmol), and 20 ml methanol was stirred for 15 min and evaporated to dryness under vacuum. The residue was dissolved in 5 ml $CH_2Cl_2$, filtered, concentrated, and diluted with 50 ml methanol. Cooling to —20°C gave yellow crystals (0.58 g, 44%). IR ($CH_2Cl_2$): $\nu$(COC) 1097, 1068 $cm^{-1}$. $^1$H NMR ($CDCl_3$): $\tau$ 4.75 (q of t, $^3J$(HH) 7 Hz, $^2J$(PH) + $^4J$(PH) 5.0 Hz, 2H, PCH), 6.70 (s, 6H, $OCH_3$), 8.38 ppm (t, $^3J$(PH) + $^5J$(PH) 14 Hz, 36H, t-Bu) (the $CH_3$ resonance is partially hidden under the t-Bu peaks). Anal.: Found: C, 38.83; H, 7.37. Calcd.: C, 39.17; H, 7.42%.

*$PtCl_2(t\text{-}Bu_2PCH_2CH_2OCH_3)_2$*

A mixture of $Na_2PtCl_4 \cdot 4\ H_2O$ (0.90 g, 1.98 mmol), $t\text{-}Bu_2PCH_2CH_2OCH_3$ (1.0 g, 4.90 mmol), and 20 ml methanol was allowed to react as in the previous procedure. A yield of 0.82 g (62%) of the yellow crystalline product was obtained from $CH_2Cl_2CH_3OH$. IR ($CH_2Cl_2$): $\nu$(COC) 1105 $cm^{-1}$. $^1$H NMR ($CDCl_3$): $\tau$ 6.12 (m, 4H, $CH_2O$), 6.63 (s, 6H, $OCH_3$), 7.64 (m, 4H, $PCH_2$), 8.52 ppm (t, $^3J$(PH) + $^5J$(PH) 13.0 Hz, 36H, t-Bu). Anal.: Found: C, 39.03; H, 7.60. Calcd.: C, 39.17, H, 7.42%.

*$PtCl_2(t\text{-}Bu_2PCO_2CH_3)_2$*

A solution of $Na_2PtCl_4 \cdot 4\ H_2O$ (1.50 g, 3.18 mmol) in 25 ml methanol was stirred while $t\text{-}Bu_2PCO_2CH_3$ (1.5 g, 7.35 mmol) was rapidly added. After stirring 1 h, solvent was removed under vacuum. The solid was dissolved in 15 ml $CH_2Cl_2$, filtered, and diluted with 150 ml methanol. Cooling to —20°C gave the light yellow crystalline product (1.61 g, 72%). IR ($CH_2Cl_2$): $\nu$(CO) 1710, $\nu$(COC) 1150 $cm^{-1}$. $^1$H NMR ($CDCl_3$): $\tau$ 6.20 (s, 6H, $OCH_3$), 8.38 ppm (t, $^3J$(PH) + $^5J$(PH) 14.2 Hz, 36H, t-Bu). Anal.: Found: C, 35.81; H, 6.05. Calcd.: C, 35.61; H, 6.23%.

*cis-$PtCl_2(Ph_2PCO_2CH_3)_2$*

A suspension of $PtCl_2(NCC_6H_5)_2$ (1.0 g, 2.12 mmol) in 20 ml n-propanol containing $Ph_2PCO_2CH_3$ (1.30 g, 5.33 mmol) was heated to reflux for 40 min. The resultant white precipitate was washed with methanol and dried under vacuum to yield 0.90 g (56%) of the product. IR ($CH_2Cl_2$): $\nu$(CO) 1730, $\nu$(COC) 1160 $cm^{-1}$. $^1$H NMR ($CDCl_3$): $\tau$ 2.15, 2.58 (m, 20H, $C_6H_5$), 6.43 ppm (s, 6H, $CH_3$). Anal.: Found: C, 44.35; H, 3.32. Calcd.: C, 44.56; H, 3.44%.

*$PtCl_2(t\text{-}Bu_2PCH_2CO_2CH_3)_2$*

A solution of $Na_2PtCl_4 \cdot 4\ H_2O$ (1.0 g, 2.20 mmol) in 30 ml methanol was treated with $t\text{-}Bu_2PCH_2CO_2CH_3$ (1.0 g, 4.59 mmol) at 25°C. After 1.5 h the suspension was filtered, and the yellow solid washed with $H_2O$ and $CH_3OH$. The product (1.45 g, 94%) was dried under vacuum. $^1H$ NMR ($CDCl_3$): $\tau$ 6.33 (s, 6H, $OCH_3$), 6.75 (t, $^2J(PH) + {}^4J(PH)$ 7.0 Hz, $^3J(PtH)$ 6.5 Hz, 4H, $PCH_2$), 8.48 ppm (t, $^3J(PH) + {}^5J(PH)$ 14.0 Hz, 36H, t-Bu). Anal.: Found: C, 37.57; H, 6.60. Calcd.: C, 37.61; H, 6.55%.

*$PtCl_2[Et_2PCH(CH_3)OCH_3]_2$*

A solution of $Na_2PtCl_4 \cdot 4\ H_2O$ (1.53 g, 3.36 mmol) and $Et_2PCH(CH_3)OCH_3$ (1.0 g, 6.76 mmol) in 40 ml methanol was stirred at 25°C for 18 h, then evaporated to dryness under vacuum. The residue was extracted with diethyl ether. Evaporation of the ether yielded an oil which crystallized upon cooling to —78°C. Recrystallization of the product from hexane at —78°C gave yellow crystals (1.0 g, 53%). The color and NMR spectrum of this product suggest that it is a mixture of *cis* and *trans* isomers. $^1H$ NMR ($CDCl_3$): $\tau$ 5.50, 5.80 [(q of d, *J* 3, 7 Hz), (q, *J* 7 Hz), 2H, CH], 6.60 (s, 6H, $OCH_3$), 7.4—8.2 (m, 6H, $CH_3$), 8.2—9.1 ppm (m, 20H, Et). Anal.: Found: C, 29.96; H, 6.13. Calcd.: C, 29.89; H, 6.05%.

*$PdCl_2(t\text{-}Bu_2PCH_2OCH_3)_2$*

A mixture of $PdCl_2(NCC_6H_5)_2$ (1.50 g, 3.92 mmol) and $t\text{-}Bu_2PCH_2OCH_3$ (1.50 g, 7.89 mmol) in 25 ml methanol was refluxed 16 h. Cooling and filtration gave the light yellow product (1.37 g, 62%). IR ($CH_2Cl_2$): $\nu$(COC) 1105 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\tau$ 5.77 (s, 4H, $CH_2$), 6.67 (s, 6H, $OCH_3$), 8.50 ppm (t, $^3J(PH) + {}^5J(PH)$ 13.0 Hz, 36H, t-Bu). Anal.: Found: C, 42.91; H, 8.45. Calcd.: C, 43.06; H, 8.25%.

*$\overline{PtCl(t\text{-}Bu_2PCH_2OCH_2)}(t\text{-}Bu_2PCH_2OCH_3)$*

A solution of $PtCl_2(t\text{-}Bu_2PCH_2OCH_3)_2$ (0.30 g, 0.46 mmol) in 5 ml decalin was heated to 175°C with a slow $N_2$ purge for 15 h. The solvent was removed under vacuum, and the residue was dissolved in 3 ml hexane, filtered, and cooled to —20°C to yield white crystals (0.17 g, 58%). The identical product was obtained from similar reactions in 2-methoxyethanol (124°C) and diglyme (138°C) within 12—18 h. IR ($CH_2Cl_2$): $\nu$(COC) 1100, 1055 $cm^{-1}$, (Nujol): $\nu$(PtCl) 260 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\tau$ 5.03 (t, $^3J(PH)$ 6 Hz, $^2J(PtH)$ 64 Hz, 2H, $PtCH_2$), 6.00 (s, $^3J(PtH)$ 24 Hz, 2H, $PCH_2$), 6.47 (d, $^2J(PH)$ 2 Hz, $^3J(PH)$ 25 Hz, 2H, $PCH_2$), 6.67 (s, 3H, $OCH_3$), 8.55 ppm (d, $^3J(PH)$ 14.5 Hz, 36H, t-Bu). Anal.: Found: C, 39.38; H, 7.45. Calcd.: C, 39.37; H, 7.38%.

*$\overline{PtI(t\text{-}Bu_2PCH_2OCH_2)}(t\text{-}Bu_2PCH_2OCH_3)$*

A mixture of $PtCl_2(t\text{-}Bu_2PCH_2OCH_3)_2$ (1.5 g, 2.32 mmol), NaI (5.1 g, 34 mmol), and 1,8-bis(dimethylamine)naphthalene (0.54 g, 2.52 mmol) in 100 ml 2-methoxyethanol was stirred at reflux (124°C) for 30 min. The yellow color of the solution faded rapidly during this period. The solvent was removed under vacuum, and the white residue was extracted with two 75-ml portions of warm hexane. The combined hexane solutions were concentrated under vacuum until

precipitation began, then cooled to —20°C. The resultant crystals were dissolved in 75 ml warm hexane and slowly cooled to —20°C to yield the pure product (1.05 g, 65%). IR ($CH_2Cl_2$): $\nu$(COC) 1100, 1060 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\tau$ 4.87 (s, $^2J$(PtH) 58 Hz, 2H, $PtCH_2$), 6.05 (s, $^3J$(PtH) 28 Hz, 2H, $PCH_2$), 6.36 (d, $^2J$(PH) 2 Hz, $^3J$(PtH) 37 Hz, 2H, $PCH_2$), 6.60 (s, 3H, $OCH_3$), 8.50 ppm (d, $^3J$(PH) 13 Hz, 36H, t-Bu); $^{13}C$ NMR ($CDCl_3$): $\delta$ 71.76 (s, $^1J$(PtC) 775 Hz, $PtCH_2$), 64.96 (d, $^1J$(PC) 28.5 Hz, $PCH_2$), 62.02 (d, $^1J$(PC) 36.0 Hz, $PCH_2$), 60.49 (d, $^3J$(PC) 11.0 Hz, $OCH_3$), 35.33 (m, $\underline{C}(CH_3)_3$), 30.69 (s, $C(\underline{C}H_3)_3$), 30.19 ppm (s, $C(\underline{C}H_3)_3$). Anal.: Found: C, 34.33; H, 6.52; I, 17.29; P, 8.74. Calcd.: C, 34.24; H, 6.42; I, 18.12; P, 8.84%.

*$\overline{Pt(NO_3)(t\text{-}Bu_2PCH_2OCH_2)}$(t-$Bu_2PCH_2OCH_3$)*

Silver nitrate (0.047 g, 0.28 mmol) in 1 ml $H_2O$ was added to a solution of $\overline{PtCl(t\text{-}Bu_2PCH_2OCH_2)}$(t-$Bu_2PCH_2OCH_3$) (0.17 g, 0.28 mmol) in 10 ml acetone. After filtration, the solution was evaporated to dryness and the residue dissolved in 2 ml warm hexane. Slow cooling to —20°C gave the crystalline product (0.10 g, 57%). $^1H$ NMR ($CDCl_3$): $\tau$ 4.95 (t, $^3J$(PH) 7.0 Hz, $^2J$(PtH) 64 Hz, 2H, $PtCH_2$), 5.91 (s, $^3J$(PtH) 13 Hz, 2H, $PCH_2$), 6.52 (d, $^2J$(PH) 2 Hz, $^3J$(PtH) 32 Hz, 2H, $PCH_2$), 6.68 (s, 3H, $OCH_3$), 8.59 ppm (d, $^3J$(PtH) 14 Hz, 36H, t-Bu). Anal.: Found: C, 37.20; H, 6.91; N, 2.12. Calcd.: C, 37.73; H, 7.08; N, 2.20%.

*$\overline{PtCl[t\text{-}Bu_2PCH_2C(O)O]}$(t-$Bu_2PCH_2CO_2CH_3$)*

A solution of $PtCl_2$(t-$Bu_2PCH_2CO_2CH_3$)$_2$ (0.20 g, 0.28 mmol) in 15 ml 2-methoxyethanol was heated to reflux for 17 h with a slow $N_2$ purge. Evaporation of the solvent under vacuum yielded a pale yellow solid. $^1H$ NMR ($CDCl_3$): $\tau$ 6.35 (s, 3H, $OCH_3$), 6.5—8.2 (multiplets), 8.53 (d, $^3J$(PH) 12 Hz, 18H, t-Bu), 8.58 ppm (d, $^3J$(PH) 12 Hz, 18H, t-Bu). Anal.: Found: C, 39.13; H, 6.76. Calcd.: C, 38.68; H, 6.60%.

*Reaction of $PtCl_2[t\text{-}Bu_2PCH(CH_3)OCH_3]_2$ upon heating*

A suspension of the metal complex (0.15 g, 0.22 mmol), NaI (0.22 g, 1.47 mmol), 1,8-bis(dimethylamine)naphthalene and (0.06 g, 0.28 mmol) in 20 ml 2-methoxyethanol was heated to reflux for 30 min, conditions which cause complete metalation of $PtCl_2$(t-$Bu_2PCH_2OCH_3$)$_2$. A sample of the solution was withdrawn and evaporated to dryness. An NMR spectrum showed only the starting complex.

A solution of $PtCl_2[t\text{-}Bu_2PCH(CH_3)OCH_3]_2$ (1.5 g, 2.22 mmol) in 25 ml 2-methoxyethanol was heated at 124°C under a slow stream of $N_2$ for 72 h. Cooling to 25°C yielded yellow crystals (0.34 g, 27%) of $PtCl_2$(t-$Bu_2PH$)$_2$, identified by its characteristic $^1H$ NMR spectrum [17]. The residue upon evaporation of the remaining solution also contained much of this complex, as observed by NMR. Anal.: Found: C, 34.79; H, 7.05. Calcd.: C, 34.41; H, 6.81%.

*Reaction of $\overline{PtCl(t\text{-}Bu_2PCH_2OCH_2)}$(t-$Bu_2PCH_2OCH_3$) with HCl*

A solution of the metal complex (0.10 g, 0.16 mmol) in 5 ml 2-methoxyethanol was treated with slowly bubbling anhydrous HCl for 10 min. The solvent was removed under vacuum and an NMR spectrum was recorded in $CDCl_3$. More than half of the metalated complex had been converted to $PtCl_2$(t-$Bu_2PCH_2OCH_3$)$_2$.

*IrHCl(t-Bu$_2$PCH$_2$OCH$_2$)(t-Bu$_2$PCH$_2$OCH$_3$)*

A suspension of [IrCl(COT)$_2$]$_2$ (0.50 g, 0.56 mmol) in 20 ml hexane was stirred with t-Bu$_2$PCH$_2$OCH$_3$ (0.74 g, 3.89 mmol) for 5 h at 25°C. The deep red solution was then filtered and concentrated under vacuum until crystallization began. Slow cooling to —20°C gave the dark red product (0.35 g, 68%). IR ($CH_2Cl_2$): $\nu$(IrH) 2310, $\nu$(COC) 1105, 1045 cm$^{-1}$; $^1$H NMR ($C_6D_6$): $\tau$ 4—7 (m, br, $CH_2$), 6.10 (s, 3H, $OCH_3$), 8.72 (d, $^3J$(PH) 12 Hz, 18H, t-Bu), 8.76 ppm (d, br, $^3J$(PH) 12 Hz, 18H, t-Bu). Anal.: Found: C, 39.61; H, 7.73. Calcd.: C, 39.51; H, 7.57%.

*Ir(CO)HCl(t-Bu$_2$PCH$_2$OCH$_2$)(t-Bu$_2$PCH$_2$OCH$_3$)*

The product from the preceding synthesis (0.30 g, 0.33 mmol) was suspended in 20 ml hexane and treated with bubbling CO for 10 min, which caused the complex to form a pale yellow solution. This was filtered and concentrated under vacuum. Cooling to —20°C gave pale yellow crystals (0.15 g, 72%). IR ($CH_2Cl_2$): $\nu$(IrH) 2190, $\nu$(CO) 1995 cm$^{-1}$; $^1$H NMR ($C_6D_6$): $\tau$ 5.0—7.1 (multiplets, 6H, $CH_2$), 6.85 (s, 3H, $OCH_3$), 1.46, 1.40, 1.37, 1.26 (all doublets, $^3J$(PH) 13 Hz, 36H, non-equivalent t-Bu), 18.0 ppm (pseudo-triplet of doublets, outer lines separated by 32.5 Hz, smaller $J$ 3 Hz, 1H, IrH); $^{13}$C NMR ($C_6D_6$): $\delta$ 64.68 (d, $^1J$(PC) 28.0 Hz, $PCH_2$), 63.78 (d, $^1J$(PC) 36.5 Hz, $PCH_2$), 60.57 (d, $^3J$(PC) 11.4 Hz, $OCH_3$), 47.62 (s, IrC), 38—34 (16 lines, 4 sets of doublets of doublets, $^1J$(PC) 20 Hz, $^3J$(PC) 3.5 Hz, four non-equivalent $\underline{C}(CH_3)_3$), 30.56 (s, $C(\underline{C}H_3)_3$), 29.72 ppm (s, $C(\underline{C}H_3)_3$). Anal.: Found: C, 39.78; H, 7.44. Calcd.: C, 39.65; H, 7.24%.

*IrHCl[t-Bu$_2$PCH(CH$_3$)OCH$_2$][t-Bu$_2$PCH(CH$_3$)OCH$_3$]*

A mixture of [IrCl(COT)$_2$]$_2$ (1.50 g, 1.68 mmol) and t-Bu$_2$PCH(CH$_3$)OCH$_3$ (1.38 g, 6.76 mmol) in 30 ml hexane was stirred at 25°C for 2 h. The suspension was filtered, concentrated under vacuum, and cooled to —20°C, yielding the dark red crystalline product (0.45 g, 26%). $^1$H NMR ($C_6D_6$): $\tau$ 3.7—6.9 (multiplets, CH and $CH_2$), 7.0, 7.1 (singlets, $OCH_3$), 8.1—8.7 ppm (multiplets, t-Bu and $CH_3$). Anal.: Found: C, 41.45; H, 7.75. Calcd.: C, 41.54; H, 7.86%.

*Ir(CO)HCl[t-Bu$_2$PCH(CH$_3$)OCH$_2$][t-Bu$_2$PCH(CH$_3$)OCH$_3$]*

A suspension of the product from the preceding synthesis (0.5 g, 0.24 mmol) in 10 ml hexane was treated with bubbling CO for about 5 min, which caused the color to change to a pale yellow. Concentrating the sample and cooling to —20°C gave the light yellow product (0.12 g, 77%). IR (hexane): $\nu$(IrH) 2160, $\nu$(CO) 1985 cm$^{-1}$; $^1$H NMR ($C_6D_6$): $\tau$ 4.5—6.5 (multiplets, 2H, CH), 7.0, 7.1 (singlets, 3H, $OCH_3$), 8.2—8.9 (multiplets, 42H, t-Bu and $CH_3$), 17.8 ppm (pseudo-triplet of multiplets, outer lines separated by 33 Hz, 1H, IrH). Anal.: Found: C, 41.63; H, 7.48. Calcd.: C, 41.60; H, 7.54%.

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